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(54) Title of the Invention: Water-soluble thickener and  
cosmetic in which same is blended

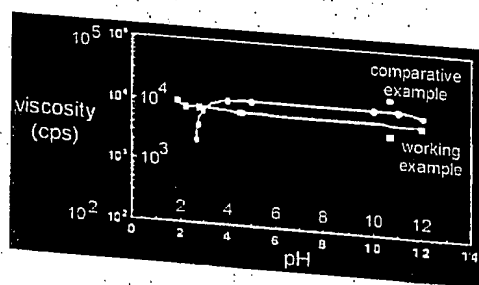
(57) Abstract

[Problem]

One problem is to provide an acid-resistant and salt-resistant water-soluble thickener that exhibits little decline in viscosity in aqueous salt solution or in the presence of acidity. Another problem is to provide a cosmetic that exhibits an excellent acid resistance and salt resistance due to the admixture therein of the water-soluble thickener and that therefore does not exhibit a slippery sensation because it is not subject to the viscosity decline and/or water separation phenomenon that can be caused by salt on body surfaces.

[Solution]

The water-soluble thickener afforded by the copolymerization of (meth)acrylic acid and/or salt thereof, (meth)acrylamidoalkylsulfonic acid and/or salt thereof, and crosslinking monomer, or by the neutralization of the resulting copolymer with base. Also, cosmetics in which said water-soluble thickener has been blended.



### Claims

[Claim 1] Water-soluble thickener afforded by the copolymerization of (meth)acrylic acid and/or salt thereof, (meth)acrylamidoalkylsulfonic acid and/or salt thereof, and crosslinking monomer, or by the neutralization of the resulting copolymer with base.

[Claim 2] The water-soluble thickener described in claim 1, that characteristically contains 45-90 mole% (meth)acrylic acid units and 10-55 mole% (meth)acrylamidoalkylsulfonic acid units and also 0.001-2.0 mole% crosslinking monomer.

[Claim 3] Cosmetic that characteristically contains water-soluble thickener according to claim 1 or 2.

### Detailed Description of the Invention

[0001]

#### Field of the Invention

This invention relates to a water-soluble thickener that exhibits little decline in viscosity in aqueous salt solution or in the presence of acidity and that is obtained by the copolymerization of (meth)acrylic acid or salt thereof, (meth)acrylamidoalkylsulfonic acid or salt thereof, and crosslinking monomer or by the neutralization of the resulting copolymer with base. This invention can be used in a broad range of applications including, for example, pharmaceuticals and cosmetics.

[0002]

This invention also relates to cosmetics into which the aforesaid water-soluble thickener has been blended. This invention can be applied to a broad range of cosmetics including, for example, skin cosmetics and hair cosmetics.

[0003]

### Description of the Prior Art

Water-soluble thickeners utilizable over a broad range of applications, including pharmaceuticals and cosmetics, can be exemplified by natural polymers such as various polysaccharides and gelatin, synthetic polymers such as polyoxyethylene and crosslinked poly(meth)acrylic acid, and inorganic minerals such as montmorillonite and silica. Among these, crosslinked poly(meth)acrylic acid offers the advantages of low cost, high thickening activity, and gelation at low additions and hence is frequently used in the pharmaceutical and cosmetic spheres.

[0004]

The aforementioned water-soluble thickeners are blended into cosmetics in particular as thickeners and stabilizers.

[0005]

### Problems to be Solved by the Invention

Dissociation of the carboxyl group in crosslinked poly(meth)acrylic acid, however, is inhibited in aqueous solutions that contain salt or that exhibit acidity  $\leq$  pH 5. This results in a major decline in viscosity and prevents gelation under these conditions, which as a consequence precludes use in recipes that require acidic conditions or a salt-containing system. This behavior can be a fatal drawback with regard to application as a gelling agent in cosmetics for which the use characteristics are a critical issue. When, for example, crosslinked poly(meth)acrylic acid is used as a thickener, the sharp decline in viscosity that occurs under acidic conditions of pH  $\leq$  5 requires a substantial increase in the addition of crosslinked poly(meth)acrylic acid under these conditions in order to maintain a satisfactory viscosity, the result of which is a deterioration in use characteristics. In addition, when a cosmetic thickened and gelled by crosslinked poly(meth)acrylic acid is applied to the skin, the salt present on the skin surface can induce separation of the water fraction and a slippery use sensation may be produced. This slippery sensation is particularly significant when such a cosmetic is used immediately after perspiration has occurred.

[0006]

The present inventors carried out extensive and intensive investigations in view of the circumstances described above in pursuit of a material that would have a high thickening

activity and a high gelation performance and would be usable in a broad range of applications including pharmaceuticals and cosmetics. As a result of these investigations, the inventors discovered that the problems cited above are solved by a water-soluble thickener obtained by the copolymerization of (meth)acrylic acid or salt thereof, (meth)acrylamidoalkylsulfonic acid or salt thereof, and crosslinking monomer and by cosmetics in which said water-soluble thickener has been blended. This invention was achieved based on this discovery.

[0007]

#### Means Solving the Problems

In specific terms, this invention provides a water-soluble thickener that exhibits little decline in viscosity even in aqueous salt solution or in the presence of acidity and that is obtained by the copolymerization of (meth)acrylic acid and/or salt thereof, (meth)acrylamidoalkylsulfonic acid and/or salt thereof, and crosslinking monomer, or by the neutralization of the resulting copolymer with base.

[0008]

This invention also provides a water-soluble thickener as described above that characteristically contains 45-90 mole% (meth)acrylic acid units and 10-55 mole% (meth)acrylamidoalkylsulfonic acid units and also 0.001-2.0 mole% crosslinking monomer.

[0009]

This invention also provides highly acid-resistant, highly salt-resistant cosmetics that contain the aforementioned water-soluble thickener and that exhibit excellent use characteristics.

[0010]

The structure and elements of this invention are described hereinafter. The copolymer used as the water-soluble thickener of this invention is obtained from (meth)acrylic acid and/or salt thereof, (meth)acrylamidoalkylsulfonic acid and/or salt thereof, and crosslinking monomer. The (meth)acrylamidoalkylsulfonic acid may be used in salt form, and the copolymerization can be carried out using just the salt or the salt in combination with the (meth)acrylamidoalkylsulfonic acid.

[0011]

The (meth)acrylamidoalkylsulfonate salt can be, for example, the alkali metal salt, the salt with ammonia, or the salt with an organic amine such as triethylamine or triethanolamine.

[0012]

The inventive water-soluble thickener can also be obtained by neutralizing the (meth)acrylamidoalkylsulfonic acid unit in the obtained copolymer with a base.

[0013]

The copolymer can be prepared by known polymerization methods such as solution polymerization, emulsion polymerization, and bulk polymerization.

[0014]

The polymerization initiator is not critical as long as it has the capacity to initiate radical polymerization. The polymerization initiation can be exemplified by benzoyl peroxide, azobisisobutyronitrile, potassium persulfate, and ammonium persulfate.

[0015]

The copolymer prepared by a method as described above may contain units from other vinyl monomers in addition to the (meth)acrylic acid and (meth)acrylamidoalkylsulfonic acid units, but only insofar as the effects of this invention, i.e., a water-soluble thickener that undergoes little decline in viscosity in the presence of acidity or in aqueous salt solution, are not impaired.

[0016]

The crosslinking monomer used in this invention must contain at least two polymerizable double bonds in each molecule, must dissolve in the reaction solvent in which the (meth)acrylic acid or salt thereof and (meth)acrylamidoalkylsulfonic acid or salt thereof are dissolved, and must have a good copolymerizability and be able to efficiently form a crosslinked structure.

[0017]

Crosslinking monomers with these characteristics can be exemplified by ethylene glycol diacrylate, ethylene glycol [di]methacrylate, diethylene glycol [di]acrylate, diethylene glycol dimethacrylate, trimethylolpropane triacrylate, N,N'-methylenebisacrylamide, N,N'-ethylenebisacrylamide, triallyl isocyanurate, and pentaerythritol dimethacrylate, which may be used singly or in combinations of two or more.

[0018]

The inventive water-soluble thickener, that is, the copolymer, preferably contains 45-90 mole% (meth)acrylic acid or salt thereof and 10-55 mole% (meth)acrylamidoalkylsulfonic acid or salt

thereof. The viscosity of the inventive water-soluble thickener is caused by extension of the molecular chain due to electrostatic repulsion based on the sulfonyl group, a strongly dissociating group, and by the development of a polymer network structure due to hydrogen bonding between the sulfonyl group and carboxyl group and between carboxyl groups. When the content of (meth)acrylic acid or salt thereof is less than 45 mole%, a satisfactory viscosity may not be obtained due to the corresponding reduction in hydrogen bond formation. When the content of the (meth)acrylic acid or salt thereof is greater than 90 mole%, i.e., when the content of the (meth)acrylamidoalkylsulfonic acid or salt thereof is less than 10 mole%, the sulfonyl group-based electrostatic repulsion and the sulfonyl group-to-carboxyl group hydrogen bonding will both decline, which can likewise result in a decline in viscosity.

[0019]

The crosslinking monomer used by this invention is preferably used at 0.001-2.0 mole% with respect to the total number of moles of (meth)acrylic acid or salt thereof and (meth)acrylamidoalkylsulfonic acid or salt thereof. The water-soluble thickener prepared using less than 0.001 mole% can exhibit a low gelation capacity. In the case of water-soluble thickener prepared using more than 2.0 mole%, the resulting elastic gelation occurring upon dispersion in water can prevent the appearance of desirable use characteristics.

[0020]

The molecular weight of the obtained water-soluble thickener should be from 100,000 to 5,000,000 and is adjusted based on the crosslinker addition and desired viscosity.

[0021]

The cosmetics afforded by the present invention are produced by the admixture therein of one or more of the water-soluble thickeners described in the preceding. The water-soluble thickener is blended therein preferably at 0.01-10 weight% and more preferably at 0.1-5 weight%.

[0022]

The water-soluble thickener blended into the cosmetic may contain units from other vinyl monomers in addition to the (meth)acrylic acid and (meth)acrylamidoalkylsulfonic acid units, but only insofar as the effects of this invention, i.e., the elaboration of a cosmetic that undergoes little decline in viscosity in the presence of acidity or in aqueous salt solution, are not impaired.

[0023]

As a function of its particular purpose, the cosmetic afforded by the present invention may contain suitable quantities, within a range that does not impair the effects of the present invention, of an oil base, surfactant, powder, humectant, ultraviolet absorber, alcohol, chelating agent, pH regulator, preservative, antioxidant, thickener, pharmaceutical, colorant, fragrance, water, and so forth.

[0024]

The method for preparing the inventive cosmetic is not critical. Cosmetic lotions, beauty lotions, and hair dyes, among others, can be prepared by dissolving the water-soluble thickener in water and using this as an aqueous base. Emulsion cosmetics can be prepared by mixing with an oil base.

[0025]

#### **Examples**

The invention is described in additional specific detail by the working examples provided below, but is not limited to these examples.

[0026]

#### **Example 1: Preparation of water-soluble thickener**

7 g 2-acrylamido-2-methylpropanesulfonic acid (corresponds to 25.7 mole%) was dissolved in 7 mL pure water, 7 g acrylic acid (corresponds to 73.8 mole%) was added, and, after cooling, 0.1 g N,N'-methylenebisacrylamide (corresponds to 0.5 mole%) was dissolved therein. A solution of 4.5 g sodium hydroxide dissolved in 13 mL pure water was added while cooling and 0.05 g potassium persulfate was subsequently added and dissolved. Otherwise, 2 g sorbitan monostearate was added to 400 mL n-hexane and was dissolved therein by raising the temperature to 35°C under a nitrogen current. The aforementioned aqueous solution was then gradually added while stirring to give an emulsion. The temperature was raised to 60°C and a reaction was carried out for 6 hours. This was followed by cooling to room temperature and removal of the oil layer by decantation. The aqueous layer was washed several times with 200 mL n-hexane and the precipitate was fractionated and dried in vacuo to give the desired copolymer (= water-soluble thickener).



[0027]

**Example 2: Preparation of water-soluble thickener**

14.5 g 2-acrylamido-2-methylpropanesulfonic acid (corresponds to 50.2 mole%), 5 g acrylic acid (corresponds to 49.8 mole%), and  $4.3 \times 10^{-3}$  g N,N'-methylenebisacrylamide were added to 20 mL pure water. 0.05 g potassium persulfate was additionally added and dissolved. The resulting solution was added dropwise to 200 mL n-hexane under a nitrogen current and a reaction was subsequently run overnight at 60°C. The n-hexane was thereafter removed by decantation and the remaining precipitate was then swelled with methanol, fractionated, and dried in vacuo to give the desired copolymer (= water-soluble thickener).

[0028]

**Example 3: Preparation of water-soluble thickener**

2.2 g 2-acrylamido-2-methylpropanesulfonic acid (corresponds to 10.3 mole%), 6.5 g acrylic acid (corresponds to 87.8 mole%), and 0.3 g N,N'-methylenebisacrylamide (corresponds to 1.9 mole%) were added to 20 mL pure water and 0.05 g potassium persulfate was then dissolved therein. Otherwise, 2 g sorbitan monostearate was added to 400 mL n-hexane and was dissolved therein by raising the temperature to 35°C under a nitrogen current. The aforementioned aqueous solution was then gradually added while stirring, the temperature was raised to 60°C, and a reaction was carried out for 6 hours. The reaction solution was subsequently cooled to room temperature and the oil layer was removed by decantation. The aqueous layer was washed several times with 200 mL n-hexane and the precipitate was fractionated and dried in vacuo to give the desired copolymer (= water-soluble thickener).

[0029]

The 400 MHz NMR chart of the water-soluble thickener prepared in Example 1 is given in Figure 1 and the FT-IR chart of this water-soluble thickener is given in Figure 2. The 400 MHz NMR was measured in deuterium oxide solvent. The chemical shifts of the detected peaks confirmed the presence of the methylene and methine protons of the acrylic acid unit and the methyl, methylene, and methine protons of the 2-acrylamido-2-methylpropanesulfonic acid unit.

[0030]

The FT-IR was measured by the KBr method. Absorptions originating with carboxylic acid were confirmed in the vicinity of  $3400\text{ cm}^{-1}$  and at  $1700\text{ cm}^{-1}$ ,  $1412\text{ cm}^{-1}$ , and  $1224\text{ cm}^{-1}$ , while absorptions originating with sulfonic acid were confirmed at  $1192\text{ cm}^{-1}$ ,  $1048\text{ cm}^{-1}$ , and  $627\text{ cm}^{-1}$ .

[0031]

The pH of a 1% aqueous solution of the water-soluble thickener synthesized in Example 2 (example) and a 1% aqueous solution of Hiviswako 105 (Wako Pure Chemical Industries, Inc.) (comparative example) was adjusted using 10 N aqueous sodium hydroxide and the viscosity at each pH was measured using a B-type viscometer at 6 rpm and  $25^{\circ}\text{C}$ . The results of these viscosity measurements are reported in Figure 3. The results in Figure 3 show that the water-soluble thickener synthesized in Example 2 maintained a stable viscosity regardless of the pH region.

[0032]

The pH of a 1% aqueous solution of the water-soluble thickener synthesized in Example 2 (example) and a 1% aqueous solution of Hiviswako 105 (Wako Pure Chemical Industries, Inc.) (comparative example) was adjusted to 3 using 1 N aqueous sodium hydroxide and the viscosity was measured at an ionic strength of 0.01 and 0.1 using an E-type viscometer at 20 rpm and  $25^{\circ}\text{C}$ . The ionic strength was adjusted using sodium chloride. The results of these viscosity measurements are reported in Table 1. It was confirmed that the water-soluble thickener synthesized in Example 2 had a salt resistance superior to that of the comparative example.

[0033]

Table 1.

	$\mu = 0.01$	$\mu = 0.1$
example	250 cps	140 cps
comparative example	72 cps	6.4 cps

[0034]

## Examples and Comparative Examples of Cosmetics

### Examples 4 and 5 and Comparative Examples 1 and 2

The results of evaluation are reported in Table 2 for the recipes of Examples 4 and 5 and Comparative Examples 1 and 2. These were O / W creams. The water-soluble thickener synthesized in Example 1 was used. The results in Table 2 confirm the excellent stability and use characteristics of the inventive cosmetics.

[0035]

Table 2.

		Example 4	Example 5	Comp. Ex. 1	Comp. Ex. 2
glyceryl monomyristate		1.0	1.0	1.0	1.0
isopropyl isostearate		1.0	1.0	1.0	1.0
liquid paraffin		8.0	8.0	8.0	8.0
$\alpha$ -hydroxycaproic acid		2.0	2.0	2.0	2.0
Hiviswako 105		—	—	0.1	0.5
water-soluble thickener		0.1	0.5	—	—
DG		5.0	5.0	5.0	5.0
ion-exchanged water		to 100	to 100	to 100	to 100
stability	50°C/1 month	+	+	×	+
	0°C/1 month	+	+	Δ	Δ
use characteristics	run off	+	+	×	×
	lack of stickiness	+	+	+	+

Stability evaluation (50°C/1 month)

- + : complete lack of separation
- Δ : very slight separation of the oil fraction
- x : substantial separation of the oil fraction

Stability evaluation (0°C/1 month)

- + : no change
- Δ : very slight gelation
- x : substantial gelation

Evaluation of use characteristics (run off, lack of stickiness)

- + : a rating of good is given by at least 6 members of a 10-person expert panel
- Δ : a rating of good is given by at least 4 members of a 10-person expert panel
- x : a rating of good is given by fewer than 4 members of a 10-person expert panel

[0036]

Example 6 and Comparative Examples 3 and 4

Table 3 reports recipes for acidic hair dyes. The water-soluble thickener synthesized in Example 2 was used. Preparation was carried out by a standard method. Table 3 reports the viscosity and pH of the individual samples that were prepared: the samples had about the same viscosity and pH values. The stability and use characteristics of the individual samples were also evaluated, and it was found that Example 6 gave excellent results. In contrast, Comparative Example 3 gelled with elapsed time and also had poor use characteristics. Comparative Example 4 suffered from a drop in viscosity with elapsed time and also had poor use characteristics.

[0037]

Table 3.

	Example 6	Comparative Example 3	Comparative Example 4
water-soluble thickener	2.0%	— %	— %
Keltrol	—	1.8	—
Hiviswako 105	—	—	4.0
benzyl alcohol	10.0	10.0	10.0
1,3-BG	10.0	10.0	10.0
Orange II	0.5	0.5	0.5
Alizuroi Purple	0.1	0.1	0.1
Naphthol Blue Black	0.2	0.2	0.2
pH regulator	suitable quantity	suitable quantity	suitable quantity
chelating agent	suitable quantity	suitable quantity	suitable quantity
fragrance	suitable quantity	suitable quantity	suitable quantity
ion-exchanged water	to 100	to 100	to 100
viscosity	25000 cps	20000 cps	23000 cps
pH	2.5	2.5	2.5

[0038]

Example 7

The recipe for a hair gel is reported in Table 4. The water-soluble thickener synthesized in Example 3 was used. Example 7, which was prepared by a standard method, was a hair gel with excellent use characteristics that did not drip off.

[0039]

**Table 4.**

	Example 7
water-soluble thickener	0.5%
Metolose 65SH-4000	0.1
EDTA-3Na·2H <sub>2</sub> O	0.03
methylparaben	0.1
polyvinylpyrrolidone	4.0
dipropylene glycol	3.0
fragrance	suitable quantity
ethanol	20.0
ion-exchanged water	to 100

[0040]

**Advantageous Effects of the Invention**

The water-soluble thickener according to the present invention provides an acid-resistant and salt-resistant aqueous thickening and gelling agent that undergoes little decline in viscosity even in aqueous salt solution or in the presence of acidity. It can be used, for example, in a broad range of applications including pharmaceuticals and cosmetics. Such a water-soluble thickener comprising a salt- and acid-resistant synthetic polymer has not previously existed for a broad range of applications including pharmaceuticals and cosmetics.

[0041]

The cosmetic provided by the present invention has an excellent acid and salt resistance and will not exhibit a slippery sensation because it is not subject to the viscosity decline and/or water separation phenomenon that can be caused by salt on body surfaces. Even in those cases where a recipe-based limitation typically exists because the stable pH region for a therein blended pharmaceutical or drug is the weakly acidic region, the inventive cosmetic will be entirely free of problems and will have an excellent stability and excellent use characteristics.

**Brief Description of the Drawings**

Figure 1 contains the 400 MHz NMR spectrum of the water-soluble thickener synthesized in Example 1.

Figure 2 contains the FT-IR spectrum of the water-soluble thickener synthesized in Example 1.

Figure 3 reports the results from measurement of the viscosity of the water-soluble thickener synthesized in Example 2 at each pH using a B-type viscometer at 6 rpm and 25°C.

Figure 1.

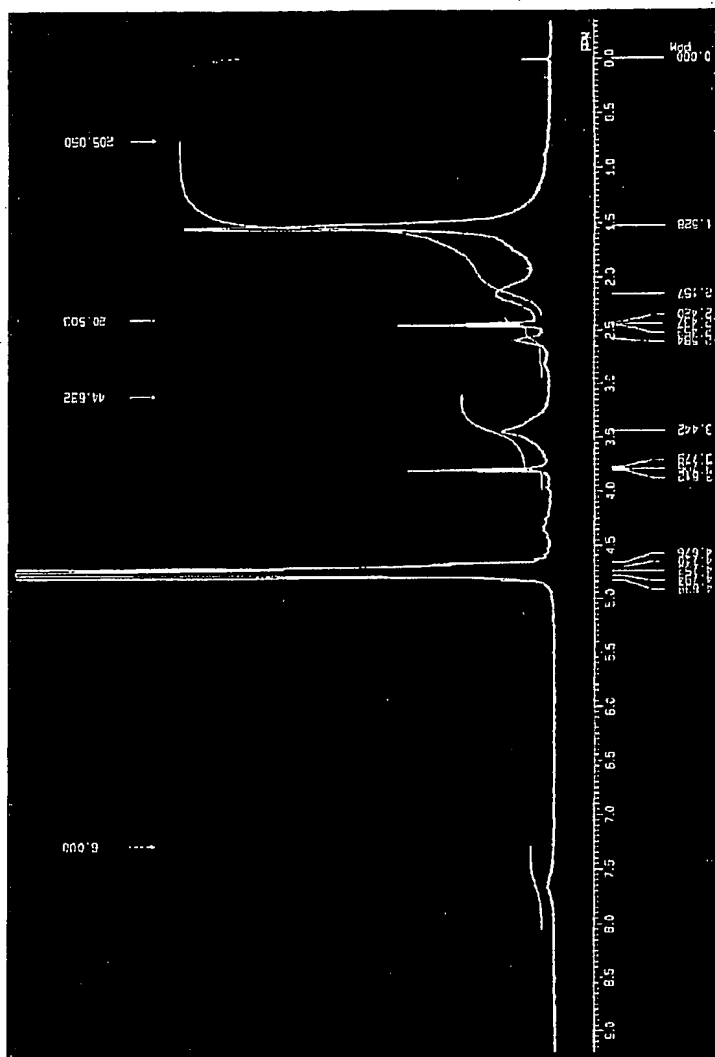




Figure 2.

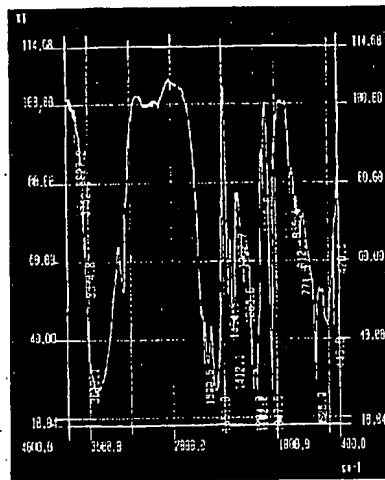
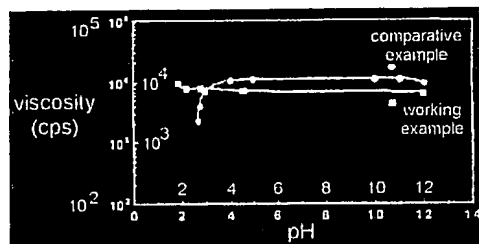


Figure 3.



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